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TECHNICAL REPORT

TR76-54-CEMEL

LIGHTWEIGHT COMBAT FOOTWEAR

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March 76

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UNITED STATES ARMY
NATICK RESEARCH and DEVELOPMENT COMMAND
NATICK, MASSACHUSETTS 01760



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <p>Expanded liquid urethane compounds with improved hydrolytic stability and good overall physical properties were developed for evaluation as lightweight combat boot outsoles.</p> <p>Liquid injection molding equipment offers a method of automating production of lightweight combat footwear based on expanded liquid urethane polymers. Mold design was improved to give better quality boots particularly flex life and better appearance because of better fit of mold to upper.</p>		

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PREFACE

This work was conducted in an effort to develop a liquid polyurethane system that will exhibit the required physical properties and that may be used for producing outsoles of 0.55 to 0.65 specific gravity by direct low pressure injection molding onto combat boot uppers. This will result in approximately a 50% reduction in the weight of the present solid outsole with a resultant decrease of approximately 25 to 30% in the overall weight of the finished footwear while maintaining the required durability and comfort.

This report describes the work performed during the 21-month period from June 1974 to March 1976. Under the supervision of Project Officer Joseph E. Assaf, US Army Natick Research and Development Command, the materials and processing studies and the development of fabrication procedures culminating in the fabrication of 50 pairs of combat footwear with an expanded polyurethane outsole were performed by Uniroyal, Incorporated, Middlebury, Connecticut under Project Reference 1T762723AH98 through Contract No. DAAK03-74-C-0153.

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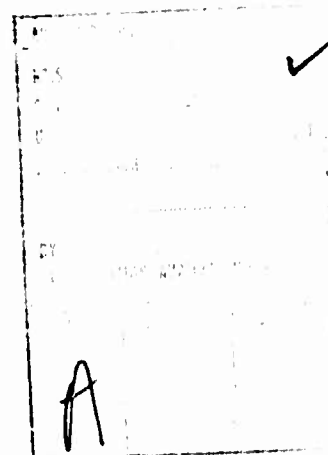


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LIGHTWEIGHT COMBAT FOOTWEAR

INTRODUCTION

The work described in this report was performed by Uniroyal, Inc., Middlebury, Connecticut. The goal of the work was to develop a 0.55 to 0.65 specific gravity, closed cell, combat footwear outsole utilizing an expanded liquid polyurethane polymer system. Physical properties must be commensurate with the requirements for this type of footwear application.

The developed outsole compound was to be capable of being direct-molded onto combat boot uppers by an automated liquid injection molding process.

The information developed under Contract No. DAAG17-71-C-0152, Lightweight Polyurethane Outsoles for Combat Footwear, dated 24 June 1971 was to be used as a guideline during the attainment of the required objectives. Work was based on conclusions reached and trends established by the previous work and continued on from that point to provide required modifications and a manufacturing process to provide direct molded combat boots.

The program was divided into two phases: The first phase involved material studies to include determination of physical properties and selection of optimum formulations as well as developing a manufacturing process suitable for fabricating footwear on automated liquid injection molding equipment. Prototype boots were also prepared. The second phase was the fabrication of 50 pair of combat footwear with a direct molded, closed cell polyurethane outsole.

Compound and processing studies during Phase one were done with urethane quasi-prepolymer systems on a Polyair Liquid-Injection-Molding-Machine. Prototype boots were produced with the same equipment and processing parameters established that were used to produce the 50 pair of combat footwear required in Phase two.

*Technical Report No. TR74-5-CE (AD773644) Lightweight Outsoles for Combat Footwear

I. Compounding Studies

The process of making a cellular polyurethane outsole consists of metering and mixing together several reactive liquid ingredients and injecting them into a mold. The liquids while still in the mold react to form a polyurethane polymer. Gas is evolved during the reaction and this causes the polyurethane to assume a cellular structure.

A. One-Shot, Quasi-Prepolymer, and Prepolymer Compounds

The reactive ingredients of a polyurethane foam system usually include an isocyanate, a hydroxyl-terminated resin, and a crosslinking agent. Flexible foam systems include a blowing agent as a source of gas for expanding the polymer that is formed. Three methods can be employed to make flexible urethane foams. The methods are the "one-shot", the prepolymer, and the quasi-prepolymer methods. In the "one-shot" method all the ingredients (hydroxyl-terminated polyol, isocyanate, cross linker, expanding agent, catalyst, and surfactant) are combined at one time to form a foam. In the other two methods part of the ingredients are pre-reacted. The prepolymer method involves the reaction of all the hydroxyl-terminated resin (polyol) with an excess of isocyanate to form an isocyanate terminated prepolymer. The prepolymer can then be subsequently mixed with the crosslinking agent, blowing agent, catalyst, and surfactant to make a foam. The quasi-prepolymer method is a combination of the "one-shot" and prepolymer methods in that a part of the polyol is prereacted with all of the isocyanate to form one of the compounds, (quasi-prepolymer or A component). The crosslinking agent, blowing agent, catalyst, and surfactant are mixed with the remaining part of the polyol to form the second component (hardener or B component). The two components (A & B) are mixed together in the proper ratio and produce a foamed material.

In all cases water was used as the blowing agent because it gives a uniform density gradient which contributes to good flex properties and the water forms urea linkages that give good toughness and increased resistance to chunking-out.

All foam work in this contract was based on formulations utilizing the quasi-prepolymer system. It has been found that these systems are particularly well suited for processing in the low pressure metering and mixing equipment for producing urethane foams (LIM equipment). The low pressure injection molding machine (LIM) can be operated most accurately by mixing two components of equal volume and equal viscosity. The quasi-prepolymer system was adopted since this type system allows mix ratios closer to one:one than either the "one-shot" or prepolymer methods.

B. Hydrolysis Resistance Requirements for Urethane Foams

Compounding studies were conducted using both polyester and polyether based systems. Polyester based foams possess excellent abrasion and flex crack resistance, however their hydrolysis resistance is not as good as the polyethers. Warehouse storage conditions to which combat footwear can be subjected over extended periods make it necessary to have a high degree of resistance to moisture without degrading the physical properties. Two approaches were followed in evaluating improvement in hydrolysis resistance of polyester type urethane foams. These included the effect of additives, and the type polyester resin spine used in the base resin. Commercially available quasi-prepolymers as well as Uniroyal prepolymers were evaluated as the "A" (isocyanate) component.

C. Additive Approach to Improved Hydrolysis Resistance

The first approach evaluated to improve the hydrolysis resistance of polyester based urethane foam was the use of an additive. Chemically, this is a poly-substituted diaryl-carbodiimide. Test slabs were made up using the liquid injection molding (LIM) equipment injecting into a 1/4" thick slab mold. The slabs were made up from two different polyester compounds. One duplicated the best polyester compound developed under the previous contract and is designated 22/A100. This compound was made up using a Uniroyal quasi-prepolymer based on ethylene glycol adipate and MDI (diphenyl methane diisocyanate) and a Uniroyal hardener (B component). The second compound involved using a commercially available quasi-prepolymer (Mondur M-420) together with a hardener (B component) composition developed by Uniroyal and is designated as 22/M-420. Change in compression deflection and change in compression set after steam autoclave aging (@248°F) was used as the criteria for comparison of hydrolytic stability.

Test results on the 22/A100 compound aged 3 hours at 248°F in the steam autoclave indicated some reduction in loss of compression deflection and reduction of compression set loss using 1% and 2% addition of carbodiimide. (Table 1) Samples run at the standard test time of 5 hours in the steam autoclave showed little improvement in retention of physical properties.

TABLE 1

POLYESTER POLYOL PHYSICAL PROPERTIES 22/A100

	A Series (3-Hour Autoclave Aging)			B Series (5-Hour Autoclave Aging)		
	22/A100	1% CD	2% CD	22/A100	1% CD	2% CD
Specific Gravity	0.75	0.75	0.74	0.75	0.76	
Abrasive Index Original After 70 Hours at 212°F	34	45	61	29	16	
	40	43	45	47	25	
Cut Growth, 50,000 Flexes Original % After 70 Hours at 212°F	0	190	0	0	0	
	0	0	0	0	0	
Compression Set @ 50% Deflection, 24 hours at R.T. Original % After Steam Autoclave	9.5*	10.1*	10.6*	8.5**	8.6**	
	15.7*	22.0*	31.1*	36.0	41.2**	
Compression Deflection @25% Deflection Original psi After Steam Autoclave	243	257	266	poor**	poor**	
	49	91	100*	sample	sample	

* - Samples slightly distorted

** - Samples distorted

In the data shown (Table 1) it should be pointed out that after aging, the samples were distorted as a result of the severe aging conditions so that accurate measurements were not possible but only an approximation could be established. Formulae are shown in Table 2.

The second polyester compound evaluated using the M-420 quasi-prepolymer (A component) and Uniroyal hardener (B component) showed no improvement in hydrolytic stability with the addition of carbodiimide in either the 3-hour or 5-hour steam autoclave test, as shown in Table 3. In addition, the samples again were distorted at the end of the aging test to the point where accurate dimensions were impossible to obtain. Formulas for these compounds are shown in Table 4.

In both the 22/A100 and 22/M-420 compounds, judging by observation of the aged samples as well as the order of magnitude test measurements for compression set and compression deflection, the physical properties after the required 5-hour steam autoclave test would not meet the requirements as stated in the contract specifications.

D. Effect of Polyester Chemical Spine on Hydrolysis Resistance

The second approach to compound improvement in polyester based urethane foams involved evaluating the effect of changing the spine of base polyester resin. The resins evaluated in the 22/A100 and 22/M-420 involved polyesters based on ethylene glycol adipate and ethylene-butylene adipate. These resins have demonstrated good flex life and abrasion resistance but marginal hydrolysis resistance based on the steam autoclave test. A series of three polyester resins with different chemical make-ups were obtained from a supplier and were described as follows:

1. Ester based on a completely saturated aliphatic material based on a dibasic acid and a long chain glycol (polyester 105).
2. Ester based on a completely saturated resin based on an aliphatic dibasic acid and mixed glycol containing some pendant alkyl groups (polyester 1015).

TABLE 2

POLYESTER POLYOL FORMULATIONS 22/A100

	(3-Hour Autoclave Aging)		(5-Hour Autoclave Aging)	
	22/A100	22/A100 1% CD	22/A100 2% CD	22/A100 1% CD
Ethylene Butylene Adipate (Polyester Resin) 2000 MW	87.57	87.57	87.57	87.57
1-4 Butanediol (chain extender)	11.26	11.26	11.26	11.26
Dabco (amine catalyst)	0.45	0.45	0.45	0.45
DC-193 (silicone surfactant)	0.375	0.375	0.375	0.375
T-9 (tin catalyst)	0.125	0.125	0.125	0.125
Water (blowing agent)	0.22	0.22	0.22	0.22
90PC02 (black pigment)	2.00	2.00	2.00	2.00
Staboxal M (carbodiimide)	---	2.03	4.07	---
	102.00	104.03	106.07	102.0
				104.03
A-100 Quasi Prepolymer (ethylene glycol adipate - MDI prepolymer 19.3% NCO)	78.6	78.6	78.6	78.6
Isocyanate Index	100	100	100	100
Quasi-Prepolymer Temp. (°F)	120	120	120	120
Hardener Temp. (°F)	130	130	130	130
Mold Temp. (°F)	120	120	120	120
Demold time - minutes	5	5	5	5

TABLE 3

POLYESTER POLYOL PHYSICAL PROPERTIES 22/M-420

	A SERIES		B SERIES	
	(3-Hour Autoclave Aging)		(5-Hour Autoclave Aging)	
	22/M-420	22/M-420 1% CD	22/M-420 2% CD	22/M-420 1% CD
Specific Gravity	0.64	0.66	0.61	0.73 0.70
Abrasive Index				
Original	85	78	71	17
After 70 Hrs. at 212°F	91	64	75	21
Cut Growth 50,000 Flexes				
Original %	0	0	0	0
After 70 Hrs. at 212°F	0	0	0	0
Compression Set @ 50% Deflection, 24 hrs. at RT				
Original %	12.8*	14.0*	12.3*	14.2*
After Steam Autoclave	12.4*	12.9	12.7*	57.6
Compression Deflection at 25% Deflection				
Original	153**	156**	142**	poor**
After Steam Autoclave	58	68	56	sample

* - Samples Slightly Distorted

** - Samples Distorted

TABLE 4

POLYESTER POLYOL FORMULATIONS 22/M-420

	(3-Hours Autoclave Aging) 22/M-420		(5-Hours Autoclave Aging) 22/M-420	
	22/M-420	1% CD	22/M-420	1% CD
Ethylene Butylene Adipate (Polyester Resin) 2000 MW	87.57	87.57	87.57	87.57
1-4 Butanediol (chain extender)	11.26	11.26	11.26	11.26
Dabco (amine catalyst)	0.45	0.45	0.45	0.45
DC-193 (silicone surfactant)	0.375	0.375	0.375	0.375
T-9 (tin catalyst)	0.125	0.125	0.125	0.125
Water (blowing agent)	0.22	0.22	0.22	0.22
90PC02 (black pigment)	2.00	2.00	2.00	2.00
Staboxal (carbodiimide)	---	2.03	---	2.03
	102.00	104.03	102.00	104.03
Mondur M-420 (Commercial)	80.25	80.25	80.25	80.25
Quasi-Prepolymer 18.9% NCO	101	101	101	101
Isocyanate Index	130	130	130	130
Quasi-Prepolymer Temperature of	120	120	120	120
Hardener Temperature of	120	120	120	120
Mold Temperature of	5	5	5	5
Demold time - minutes				

3. Ester based on partially aromatic acids and containing long chain glycol segments which lower ester group density (polyester 1019).

These resins are in the 2000 molecular weight range. This molecular weight has shown to be a good balance between good physical properties and good processing characteristics and was used in both the polyester and polyether evaluations.

Prepolymers were made with each of these resins using a two-step isocyanate addition process. The initial isocyanate addition brings the amount of free isocyanate (di phenyl methane diisocyanate-MDI) to approximately 10% and the second addition brings the free isocyanate (NCO) to approximately 20%. The same base resin was used in both the quasi-prepolymer (A component) and the hardener (B component).

Test slabs were made using the LIM equipment to meter and mix the compounds. The compounds were identified as 105, 1015, and 1019 and were run with and without a 1% addition of carbodiimide. Test results and appearance after autoclave aging indicated the 1019 to be the most hydrolysis resistant of the three resins. The addition of carbodiimide did not significantly improve resistance to 5-hour steam aging at 248°F. Samples that were steam-aged still distorted to the point where accurate measurement was not possible, but an approximation could be obtained. The 1019 samples distorted the least. Compression set after steam aging was lowest on the 1019 samples although the compression deflection was reduced. Physical test data are shown in Table 5, and formulas in Table 6. It appears that the base polyester spine is the controlling factor in hydrolysis resistance as measured by the steam autoclave test and that an additive such as carbodiimide has at best a marginal effect.

E. Polyester Package System Foam

Package systems for urethane foam are available from a number of commercial suppliers. One that has shown promise was included in this series for evaluation. It is a polyester based on adipate polyester polyols and coded 3-35. In a package system the materials are supplied as a completely formulated system in two components and in this case the same as described earlier for a quasi-prepolymer system. Sample slabs were made up and tested. Results are included in Table 7, and the mix ratios are shown in Table 8. The samples as taken from steam autoclave aging had only a very slight distortion indicating good hydrolysis resistance, and the change in compression set and compression deflection values after the autoclave aging indicated good resistance. The processing on the LIM mixing equipment was good in that the compounds mixed and cured well and produced good quality foam pieces.

TABLE 5
POLYESTER POLYOL PHYSICAL PROPERTIES 105, 1015, and 1019

	<u>105</u>	<u>105 1% CD</u>	<u>1015</u>	<u>1015 1% CD</u>	<u>1019</u>	<u>1019 1% CD</u>
Specific Gravity	0.77	0.77	0.76	0.75	0.76	0.72
Abrasive Index						
Original	20.3	19.0	--	16.0	17.6	14.7
After 70 Hrs. at 212°F	31.1	31.9	--	16.5	34.6	25.0
Cut Growth, 50,000 Flexes						
Original %	240	0	0	0	0	0
After 70 Hrs. at 212°F	0	0	0	110	0	0
Compression Set at 50% Deflection 24 Hrs. at RT						
Original %	27.7	27.1	35.5	36.9	18.5	19.7
After Steam Autoclave	50.4*	64.7*	59.5*	71.2*	27.5*	28.8*
Compression Deflection at 25% Deflection						
Original psi	poor sample	poor sample	138	148	172	166
After Steam Autoclave			147*	157*	115*	120*

* - Sample Distorted

TABLE 6

POLYESTER POLYOL FORMULATIONS 105, 1015, and 1019

	105	105 1% CD	1015	1015 1% CD	1019	1019 1% CD
Polyester 105 (Polyester Resin)	87.57	87.57				
Polyester 1015 (Polyester Resin)			87.57	87.57		
Polyester 1019 (Polyester Resin)						
1-4 Butanediol	11.26	11.26	11.26	11.26	87.57	87.57
Dabco	0.45	0.45	0.45	0.45	11.26	11.26
DC-193	0.375	0.375	0.375	0.375	0.45	0.45
T-9	0.125	0.125	0.125	0.125	0.375	0.375
Water	0.220	0.220	0.220	0.220	0.125	0.125
90PC02	2.0	2.0	2.0	2.0	0.220	0.220
Staboxal	---	2.03	---	2.03	2.0	2.0
					---	2.03
	102.00	104.03	102.00	104.03	102.00	104.03
Quasi-Prepolymer 105/MDI - 19.8% NCO	77.3	77.3				
Quasi-Prepolymer 1015/MDI - 19.8% NCO			77.3	77.3		
Quasi-Prepolymer 1019/MDI - 19.8% NCO					77.3	77.3
Isocyanate Index	101	101	101	101	101	101
Prepolymer Temp. °F	140	140	140	140	120	120
Hardener Temp. °F	140	140	140	140	130	130
Mold Temp. °F	120	120	140	140	120	120
Demold time - minutes	5	5	5	5	5	5

TABLE 7

POLYESTER POLYOL PHYSICAL PROPERTIES PCP and 3-35 (Pkg. System)

	<u>PCP</u>	<u>3-35</u>
Specific Gravity	0.70	0.72
Abrasive Index		
Original	29	34
After 70 Hours at 212°F	50	26
Cut Growth 50,000 Flexes		
Original %	0	50
After 70 Hours at 212°F	0	0
Compression Set at 50% Deflection, 24 Hours at RT		
Original %	11.9	6.3
After Steam Autoclave	35.8*	15.8
Compression Deflection at 25% Deflection		
Original psi	156	225
After Steam Autoclave	154*	180

* - Slightly Distorted Samples

TABLE 8

POLYESTER POLYOL FORMULATIONS PCP AND 3-35 (Pkg. System)

	<u>PCP</u>	<u>3-35</u>
Polycaprolactone (Polyester Resin)	87.57	
1-4 Butanediol	11.26	
Dabco	0.45	
DC-193	0.375	
T-9	0.125	
Water	0.220	
90PC02	2.0	2.0
3-35 Resin (Polyester Hardener)	--	100.0
	<u>102.00</u>	<u>102.00</u>
Quasi-Prepolymer PCP/MDI 19.7% NCO	77.7	
Quasi-Prepolymer 3-35		92.1
Isocyanate Index of	101	100
Prepolymer Temp. of	120	90
Hardener Temp. of	120	130
Mold Temp. of	130	120
Demold Time- minutes	5	4

F. Polycaprolactone Resin Based Foams

Another type of base resin was included in the evaluation of polyesters. These resins called polycaprolactones have some advantages over conventional polyesters in that they have low acid number and low water content as originally made. They offer improved low temperature properties and improved hydrolytic stability while retaining good overall properties. A commercially available polycaprolactone, 2000 molecular weight, was made up as a quasi-prepolymer system. The same prepolymer making conditions were used as on the conventional polyesters described previously, and the free isocyanate content was approximately 20%. The hardener (B component) was also based on polycaprolactone resin. The compound was identified as PCP. Foam slabs were made up for testing and the results are included in Table 7 and the formula is in Table 8. Even though there was some distortion of the samples exposed to the steam autoclave test it was less than any of the other conventional polyester-based foams tested with the exception of the package system. The test data indicated improved hydrolytic stability, but once again precise values could not be obtained because of sample distortion.

G. Review of Polyester Based Foam Compound Properties

At this point the polyester compounds were reviewed to determine which appeared to be the best candidates for the combat boot outsole application. The ester based foams as a class have good abrasion and flex characteristics. Because of concern about the aging of these type compounds, particularly under high humidity conditions, preliminary screening was concentrated on resistance to hydrolysis aging. Only trends could be indicated because of the severe aging conditions required in the steam autoclave test and observation of the condition of aged samples became an important consideration in evaluation. Based on physical test data, sample appearance, and feel, and on how a given compound processed on the LIM equipment (including supply conditions, uniformity of mix, mold fill and cure), two compounds were picked for further study. These were the polycaprolactone and the package ester system 3-35.

H. Polyether Based Compound Evaluation

Work was now directed towards evaluation of polyether based compounds. Initial evaluation of polyether based foams was done using PTMG (poly tetramethylene ether glycol) as the base polymer. This polyether was chosen since this polymer has demonstrated its superior properties in urethane elastomers requiring excellent hydrolytic stability as well as good overall toughness. A quasi-prepolymer system was

made up utilizing MDI (diphenyl methane diisocyanate) as the isocyanate component. Compounds with three different mole ratios varying the amounts of PTMG, MDI and chain extender (1-4 butanediol) were made up, and the same procedure as used in the polyester evaluation of formulating an A component composed of the quasi-prepolymer and a B component containing the balance of the ingredients (PTMG, 1-4 butanediol, catalyst, water, silicone surfactant and pigment) was used. A two-thousand molecular weight resin was used based on previous data showing this has the best balance of overall properties for this application.

To identify the mole ratios, numbers indicating the ratio of each reactive ingredient are written in a sequence starting with PTMG and followed by chain extender (1-4 butanediol), water, and MDI. Therefore, a 1.0-2.5-0.3-3.8 is composed of 1 mole of PTMG, 2.5 moles of 1-4 butanediol, 0.3 mole of water and 3.8 moles of MDI. The first series of foams was made from compounds 1.0-2.5-0.3-3.8 and 1.0-2.0-0.3-3.3 and 1.0-1.7-0.2-2.9. The compounds are listed in order of decreasing hardness accomplished through the reduction of chain extender. All three compounds showed good resistance to hydrolysis as indicated by the low compression set increase and low loss of compression deflection indicated by the physical test results in Table 9. Formulas are shown in Table 10. The samples showed only slight distortion but enough to cause some error in final measurement. It was decided to go with the intermediate amount of chain extender to get the best balance of properties including abrasive-index and flexing. Processing on the LIM equipment also favored the intermediate 1.0-2.0-0.3-3.3 compound. A series was then run varying the isocyanate index, which is a number indicating the amount of isocyanate available to react either over or under the stoichiometric amount required by the compound. An index of 100 represents the stoichiometric amount. The index was varied from 98 to 105. The physical test results on slabs made on the LIM equipment indicate an index of approximately 103 would be a good compound for the outsole application. Loss of compression deflection and compression set increase after autoclave aging were low, and abrasion and flex properties were good. Physical test data is shown in Table 11 and formulas in Table 12. The PTMG based compound selected for further evaluation is the 1.0-2.0-0.3-3.3 at a 103 isocyanate index.

Included in these Tables (11 and 12) are data on a package polyether system offered commercially based on polypropylene glycol coded PPG. This is a quasi-prepolymer system and run on the LIM as an A and B component. Physical test data indicated reasonably good abrasion and flex properties but hydrolysis resistance was not nearly as good as the PTMG based ether systems. The samples for compression set were distorted to the

TABLE 9

**POLYETHER POLYOL PHYSICAL PROPERTIES
VARYING MOLE RATIO PTMG COMPOUNDS**

	<u>1.0-2.5-0.3-3.8</u>	<u>1.0-2.0-0.3-3.5</u>	<u>1.0-1.7-0.2-2.9</u>
Specific Gravity	0.78	0.70	0.69
Abrasive Index			
Original	25.3	19.6	14.7
After 70 Hours at 212°F	63.7	32.5	38.5
Cut Growth % 50,000 Flexes			
Original %	900	240	100
After 70 Hours at 212°F	30	0	0
Compression Set at 50% Deflection, 24 Hours at RT			
Original %	4.2	4.3	3.9
After Steam Autoclave	16.37*	22.1*	10.67*
Compression Deflection at 25% Deflection			
Original psi	328	150	191
After Steam Autoclave	269*	134*	150*

* - Slight Distortion of Sample

TABLE 10

**POLYETHER POLYGL FORMULATIONS
VARYING MOLE RATIO PTMG COMPOUNDS**

	<u>1.0-2.5-0.3-3.8</u>	<u>1.0-2.0-0.3-3.3</u>	<u>1.0-1.7-0.2-2.9</u>
PTMG (Polytetramethylene ether glycol)	51.5	57.9	63.0
1-4 Butanediol	11.2	9.0	7.6
Water	0.27	0.27	0.18
DC-193	0.21	0.21	0.20
Dabco WT (catalyst)	0.315	0.315	0.515
T-12 (catalyst)	0.006	0.006	0.006
90PC02 (pigment)	0.820	0.820	0.820
	<hr/>	<hr/>	<hr/>
	64.321	68.521	72.121
Quasi-Prepolymer PTMG/MDI - 14.52% NCO	95.5	83.3	72.8
Isocyanate Index of	100	100	100
Prepolymer Temp. °F	165	165	165
Hardener Temp. °F	165	165	165
Mold Temp. °F	165	165	165
Demold time - minutes	10	10	10

TABLE 11
POLYETHER POLYOL PHYSICAL PROPERTIES
VARYING ISOCYANATE INDEX PTMG AND PPG

Isocyanate Index	PTMG- 1.0-2.0-0.3-5.3				PPG
	98	100	103	105	
Specific Gravity	0.73	0.70	0.70	0.72	0.61
Abrasive Index					
Original	23.4	19.6	50.5	20.1	34.0
After 70 Hours at 212°F	66.5	32.5	43.2	60.0	31.0
Cut Growth 50,000 Flexes					
Original %	900	240	30	40	0
After 70 Hours at 212°F	0	0	0	0	0
Compression Set at 50% Deflection, 24 Hours at RT					
Original %	3.9	4.2	3.8	4.0	14.5
After Steam Autoclave	27.5*	22.1*	15.5*	19.1*	--**
Compression Deflection at 25% Deflection					
Original psi	195	150	169	191	148
After Steam Autoclave	127*	134*	134*	132*	39*

* - Slight Distortion of Sample

** - Distorted Sample

TABLE 12
POLYETHER POLYOL FORMULATIONS
VARYING ISOCYANATE INDEX IN PTMG COMPOUNDS AND PPG

	<u>PTMG</u>	<u>(1.0-2.0-0.3-3.3)</u>				<u>PPG</u>
PTMG (polytetra methylene ether glycol)	57.9					
1-4 Butanediol	9.0					
Water	0.27					
DC-193	0.21					
Dabco WT (catalyst)	0.315					
T-12 (catalyst)	0.006					
90PC02 (pigment)	0.820					2.0
PPG (Pkg. System)						100.0
	<u>68.521</u>	<u>68.521</u>	<u>68.521</u>	<u>68.521</u>	<u>68.521</u>	<u>102.0</u>
Quasi-Prepolymer PPG						<u>45.1</u>
Quasi-Prepolymer						
PTMG/MDI - 14.52% NCO	81.6	83.3	85.8	87.5		
Isocyanate Index of	98	100	103	105	100	
Prepolymer Temp. °F	165	165	165	165	80	
Hardener Temp. °F	165	165	165	165	80	
Mold Temp. °F	165	165	165	165	120	
Demold time - minutes	10	10	10	10	5	

point that meaningful data could not be obtained. Loss of compression deflection was very noticeable. It was decided to use the PTMG compound as the best polyether based compound for the combat boot outsole.

I. Review of Physical Properties of PTMG, PCP, and Package System Foams

After reviewing the test data, test sample condition, chemical composition of the compounds evaluated and processing characteristics, it was decided the best candidates to date were the PTMG (1.0-2.0-0.3-3.3), the polycaprolactone, and the commercially available polyester package system (ester package).

A new series of test slabs with these compounds duplicating the earlier formulations were made up on the LIM, and the full range of tests shown in the contract as specifications in Table 1 were run. Results are listed in Table 13. The specific gravity of the samples made in $\frac{1}{4}$ "-thick slabs are somewhat higher than that shown in the tentative specification. The higher gravity results in higher Shore A hardness readings and higher compression deflection values. None of the samples gave an abrasive index of 70. We have found no specific correlation of the abrasive index and actual wear results. This is because the test was originally designed for solid rubber-like materials that are thermal-set rather than cellular urethanes. Excellent wear characteristics have been obtained on cellular urethane outsoles with an abrasive index figure well below the 70 minimum.

Compression set figures based on the actual percent set are felt to be acceptable. The percent change can be misleading in that a high original set with only minor changes after aging shows as acceptable, whereas a low initial set with a small increase in set after aging shows as being out of specification, even though the aged set percent passes the original requirement. Compression deflection values, after steam autoclave aging, are over the allowable percent change, but as pointed out before, the steam autoclave test at 248°F is felt to be too severe and causes the foam samples to distort giving inaccurate readings. These high temperatures can actually destroy some of the chemical linkages and are so far above any temperature and humidity condition that will be met in service that the validity is questionable. In spite of the severe aging conditions, the samples were examined after measuring the test values, and judging by feel, good foam integrity was indicated.

The tests involving low temperature properties did indicate that the package system ester is sensitive to low temperatures. Both hardness change and particularly increase in compression deflection at 0°F were significant. Since combat boots are

TABLE 13

PHYSICAL TEST RESULTS vs. TABLE 1 SPECIFICATION

Property	Spec.	PTMG (1.0-2.0-0.3-3.3)		PCP	Ester Pkg. 3-35
1. Specific Gravity	0.65 max	0.72		0.71	0.71
2. Water Pickup %	3.0 max	1.26		2.76	6.12
3. Hardness, Shore A					
Original	55 \pm 5	67		64	68
After 70 Hr/212°F	not more than 10 PT chg.	55		49	60
Hardness chg. @ 0°F	not more than 15 PT chg.	70		73	88
4. Abrasive Index					
Original	70 min.	29.4		22.1	29.9
After 70 Hr/212°F	70 min.	35.7		18.7	38.6
5. Compression Set @ 50% Deflection; 24 hrs. @ RT					
Original %	25 \pm 5	9.3		8.8	5.3
After Steam Autoclave %		14.2*		31.4*	19.9
% Change	20	52.6		256.8	275.4
6. Cut Growth 50,000 Flexes					
Original %	200 max.	0		0	140
After 70 Hrs/212°F/%	200 max.	50		0	0
7. Compression Deflection @ 25% Deflection					
Original psi	150 \pm 10	272		208	227
After Steam Autoclave psi		180*		138*	160
% Change	20 max.	34		34	30
Original					
After 1 Hr. @ 0°F		249		220	255
% Change	15% max.	238*		175*	520
		5		20	104

* - Slightly Distorted Samples

certain to be exposed to temperatures in this range, this could cause problems in stiffness and traction.

At this time, to aid in the final selection of outsole compounds for the 50 pair of combat boots, prototype boots for forced wear test were made up from the three selected compounds.

II. Prototype Boots

Prototype boots with outsoles made from the PCP, PTMG, and the package polyester system were made up using the LIM equipment. The formulas were the same as in the Tables and specific gravity was 0.55 to 0.63. These boots were forced-wear-tested over asphalt and concrete surfaces. After 400 miles there were no flex cracks or chunking out. Some wear was evidenced on the extreme toe and heel and the wear varied with the individuals and their styles of walking. All three compounds held up well.

To improve the wear characteristics of the combat boot outsole, an innovation in urethane outsole molding was tried. This involved making an insert piece out of solid urethane elastomer that fits into the heel of the outsole. The insert is molded and cured as a separate operation. Then, when the urethane foam outsole is to be molded to the leather upper, the insert piece is placed in the outsole mold cavity over locating pins to hold it in position during the injection of the outsole foam compound. The foam is injected by the LIM equipment, and after foaming and cure is complete, the boot is stripped and the solid insert is an integral part of the outsole. The design and location of the insert is shown in Figure 1. The insert mold configuration and construction is shown in Figure 2. The insert formulation and properties are shown in Table 14.

Boots made with and without inserts were compared on forced walk test and the boots with inserts showed less heel wear.

Considering the results of physical tests, examination of samples after aging, processing characteristics including flow, cure, handling ease, as well as the results of the forced wear test on the prototype boots, it was decided to make the 50 pair of service test boots from the PCP and PTMG compounds. Twenty-five pair were made from each compound.

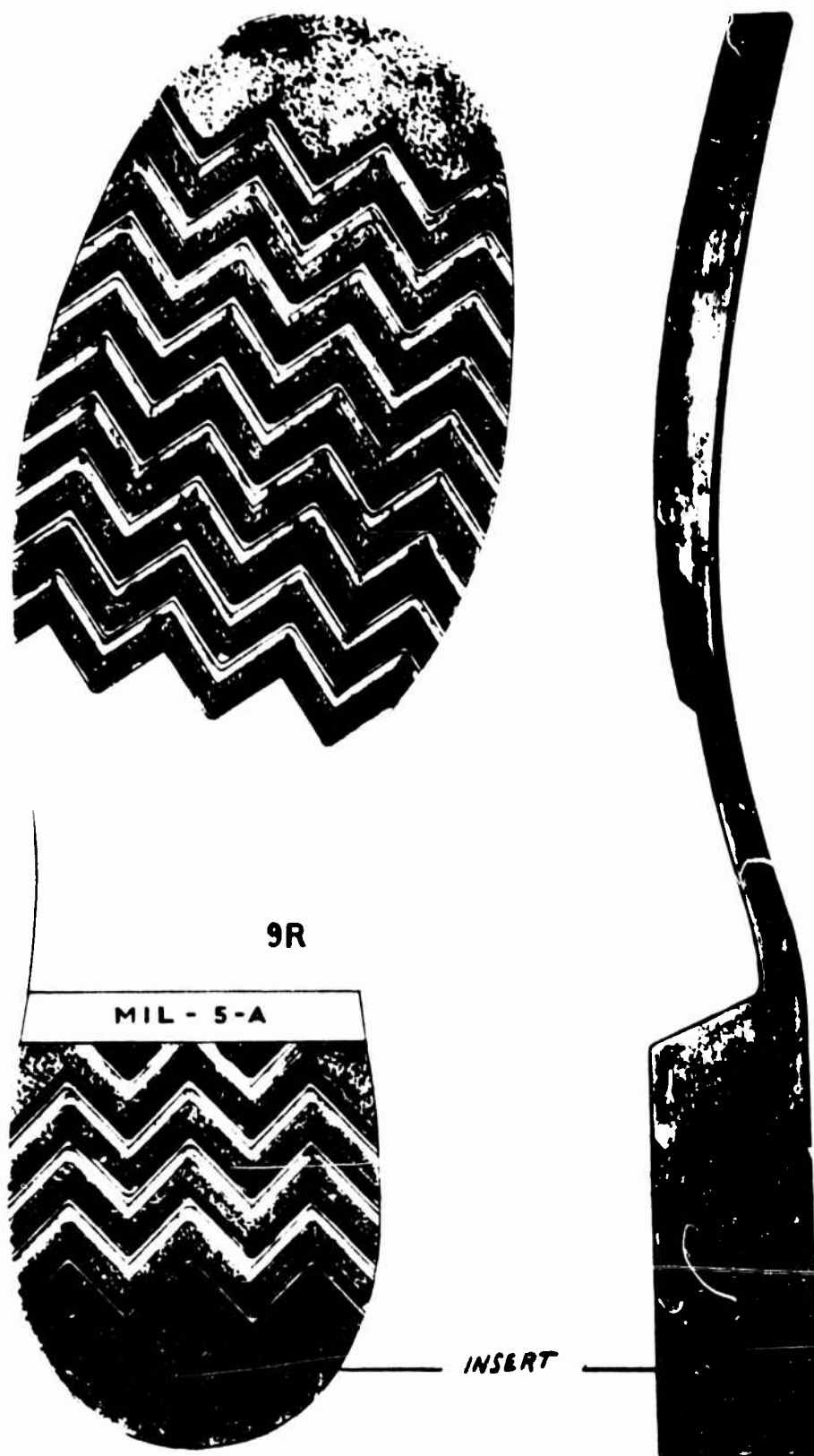


FIGURE 1
DESIGN AND LOCATION
OF INSERT
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TABLE 14
INSERT FORMULATION AND PROPERTIES

<u>Ingredient</u>	<u>Parts</u>
Ethylene Glycol Adipate (Polyester Resin)	84.23
1-4 Butanediol	13.22
Dabco	0.46
Metasol 57 DPG (catalyst)	0.12
T-12	0.02
90PC02	1.95
	<hr/>
	100.00
Quasi-Prepolymer (20.3% NCO)	
Ethylene Glycol Adipate/MDI	80.9
Index	103.5
Quasi-Prepolymer Temp. °F	120
Hardener Temp. °F	120
Mold Temp. °F	125
Demold Time - minutes	5
<u>Properties</u>	
Abrasive Index (NBS)	144.3
Shore A	83

III. Processing Studies

A. LIM Mixing Equipment

LIM foam mixing equipment was used for compound mixing and molding evaluation, production of prototype boots, and the production of 50 pair of boots. The equipment used was made by either Polyair Machinebau or Desma-Werke, and the basic operating principles of each are similar. The equipment is a foam mixing unit capable of supplying two components to a mixing head. The components are supplied from temperature controlled supply pots. Metering of the individual component streams is accomplished by the use of close tolerance gear pumps which give a high degree of accuracy. These pumps are tied together by either a common drive chain or intermeshing gears that are controlled by the speed of the main drive gear which regulates total thru-put (Figure 3). Mixing is accomplished by passing the ingredients through a high shear mixer with the mixing screw turning at 18,000 RPM (Figure 4). The mixed compound is then injected into a closed mold in a mold station. The entire mixing unit carriage can be moved forward and back by an air cylinder so that the compound can be injected in the forward position and retracted so that the mixing head can clean itself.

B. Mold Station and Mold Design

The mold is held in a mold station that has a temperature controlled platen on which the outsole mold rests. Above the mold is a piston or mechanical device for raising and lowering the last (or foot form) on which the leather upper is placed before being brought down in contact with the outsole mold to form the top section of the cavity into which the foam will be injected. The bottom section of the mold is comprised of a split upper ring and an outsole plate (Figures 5 & 6). The outsole plate of the new mold was patterned from a current issue combat boot with a modified Chevron design supplied by the Project Officer. The outsole rings have bolted on top a sealing ring with an embossed stitchline to simulate a stitched-on outsole appearance. After examining the mold used on the previous contract, changes were made in the new mold cavity dimensions in that the overall length was increased 3.5mm to be sure the outsole extended beyond both the heel and toe so the leather is protected from scuffing. The out-sole plate was revised so that there is a more rounded contour at the bottom of the Chevron groove to help prevent initiation of flex cracking. The radius at the breast of the heel was also increased to minimize any tendency to flex crack. The arch section was modified to give more foam over the metal shank. In the boots made on the previous contract there were some signs of cracking caused by the shallow depth of the metal shank from the surface.

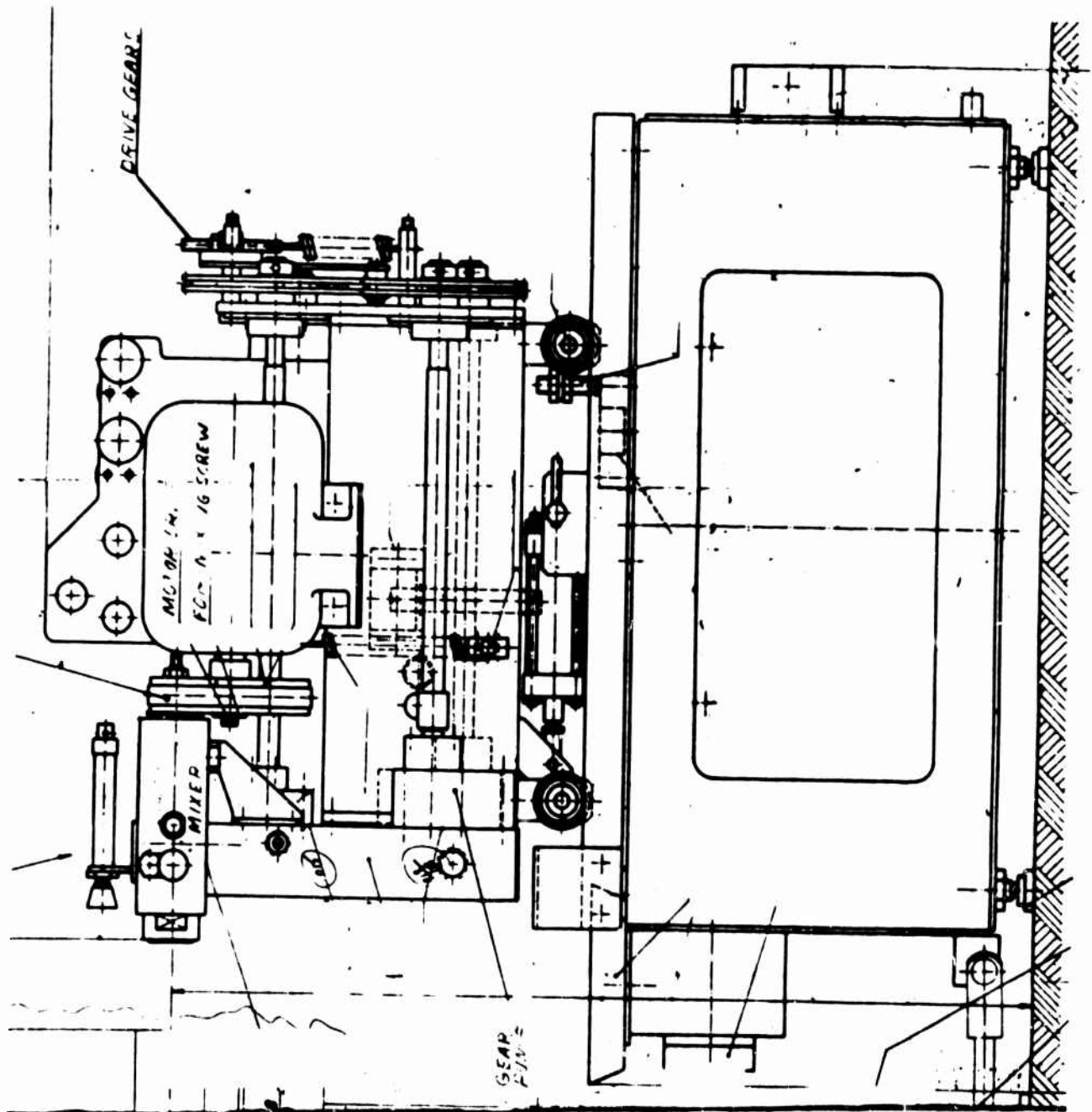


FIGURE 3
SIDE VIEW LIM INJECTOR

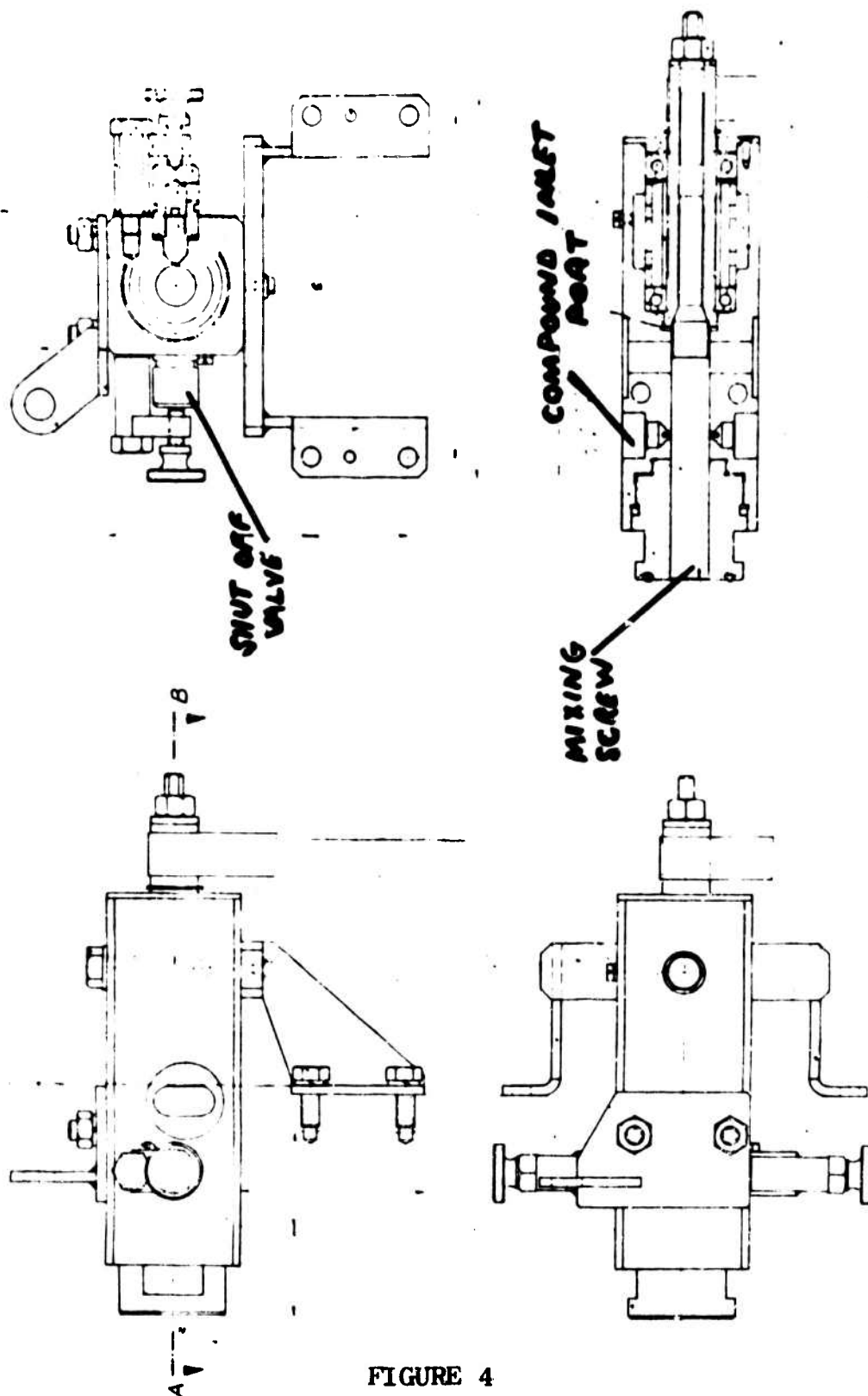


FIGURE 4
LIM MIXING HEAD

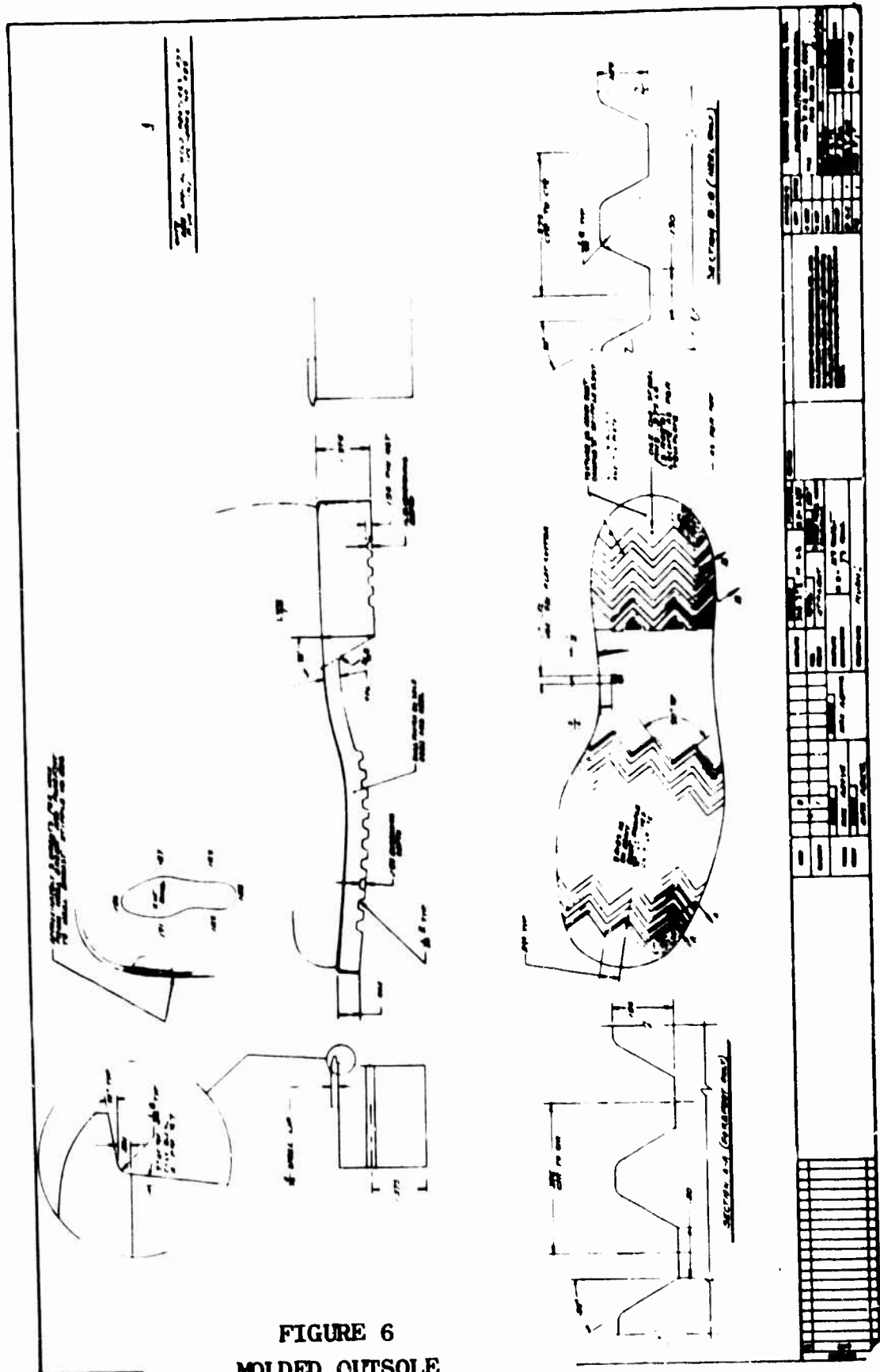


FIGURE 6
MOLDED OUTSOLE
CONFIGURATION

The sealing rings were worked down to be sure a good fit to the lasted leather upper was attained. This minimizes any foam leakage and gives a good sharp seal line that gives a good appearance and minimizes any buffing required for flash removal. After optimizing the design for good performance and fit, work was done on the alignment mechanism so that exact mating of the lasted upper to the top mold surface sealing rings can be obtained on a repetitive basis. Boots molded with this new design mold were acceptable in appearance and function and good quality boots were produced.

C. Compound Processing

Based on the results of mixing and metering a variety of urethane compounds of varying viscosities and ratio requirements, the LIM equipment performed well in making good quality foam on a repetitive basis. Adjustments are easily made, and with minimum maintenance a consistent flow of compound to the mixing head is attained. Process requirements vary with each compound, but by modification of compound or adjustments of equipment, a proper setting was developed and good test panels and boot outsole soles made. This equipment definitely lends itself to automated production techniques.

D. Process Steps

The following outline covers the processing sequence required to produce a lightweight combat boot composed of a stitched leather upper and injection molded urethane foam outsole.

Heat resin and quasi-prepolymer to melt temperature

Mix B component - resin, crosslinker, surfactant, catalyst, blowing agent and pigment. stir 15 minutes.

Deliver B component to LIM equipment

(Transfer to supply pot set at supply temperature)

Deliver A component to LIM equipment

(Transfer to supply pot set at supply temperature)

Clean mix head

Set proper ingredient ratio on LIM equipment

Check ratio in cup shot - adjust if required

Check cup batch for proper mix and cure

Last leather upper

Join filler block and steel shank

Apply filler-block, steel-shank assembly to leather upper bottom with hot melt adhesive

Close outsole rings (set at proper temperature)

D. Process Steps (continued)

Apply mold release
Position last on upper rings
Inject foam
Cure foam
Open outsole rings
Retract last
Strip complete boot
Trim boot
Apply finish coat
Inspect and pack

IV. Production of Fifty Pair of Wear Test Boots

During Phase II, fifty pair of combat boots were fabricated on LIM equipment using the modified Chevron outsole mold. Twenty-five pair were made using the PTMG based compound (1.0-2.0-0.3-3.3) and the remaining twenty-five pair were made using the polycaprolactone based compound (PCP). Approximately half of each type had an insert incorporated (in the heel area) made of the compound described previously. The boots range in specific gravity from 0.60 to 0.70. These figures were obtained by subtracting out the weight of all the individual components except the outsole from the total boot weight and then calculating based on the known mold volume. Test panels were made at the same time the boots were being processed and were delivered with the wear test boots. Conditions of making and the weights of each boot are included in Table 15. In Table 15, it should be pointed out, the molded boot weight does not include the weight of the finish coating, and the total weight therefore is increased by approximately 30 grams per boot. This is in excess of what is considered an average amount on a production standard boot by 15 to 16 grams per boot. Also in the case of the boots made with inserts an allowance is made in the figure used for the volume of the mold so that the Specific Gravity figure represents only the expanded portion of the outsole.

Test panels ($\frac{1}{4}$ " slabs) made during boot processing were tested, and results listed in Table 16. Physicals indicate good overall quality foam, and adhesion of the urethane foam to the leather uppers was very good exceeding the minimum specification by from 15 to 50 pounds pull.

Data Applicable To The Fifty Pair of Combat Boots (Phase II)

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Table 15 (continued)

Compound	Boot Code	Total Boot Weight Grams	Molded Boot Weight Grams	Upper Weight Grams	Outsole Weight Grams	Outsole Specific Gravity	Insert
P-12	L	679	647	401	246	0.644	No
	R	684	657	399	258	0.694	No
P-13	L	686	655	404	251	0.675	No
	R	661	642	400	242	0.650	No
P-14	L	696	670	414	256	0.670	No
	R	659	627	404	223	0.599	No
P-01S	L	708	667	429*	238	0.642	Yes
	R	703	664	422*	242	0.70	Yes
P-02S	L	699	658	420*	238	0.642	Yes
	R	700	660	419*	240	0.665	Yes
P-03S	L	707	666	426*	240	0.647	Yes
	R	708	668	430*	238	0.659	Yes
P-04S	L	697	653	415*	240	0.647	Yes
	R	660	618	416*	202	0.559	Yes
P-05S	L	699	654	417*	237	0.639	Yes
	R	696	652	420*	232	0.643	Yes
P-06S	L	709	663	431*	233	0.628	Yes
	R	700	655	420*	235	0.651	Yes
P-07S	L	690	645	411*	234	0.631	Yes
	R	692	647	412*	235	0.651	Yes
P-08S	L	684	635	404*	231	0.623	Yes
	R	694	645	413*	232	0.643	Yes
P-09S	L	708	661	427*	234	0.631	Yes
	R	709	661	421*	240	0.665	Yes
P-10S	L	708	675	431*	244	0.658	Yes
	R	699	668	423*	245	0.678	Yes
P-11S	L	686	653	409*	244	0.658	Yes
	R	687	656	419*	237	0.656	Yes

* - Includes insert weight and in specific gravity computation allowance is made for insert volume

Table 15 (continued)
Data Applicable to Fifty Pair of Combat Boots (Phase II)

Table 15 (continued)

Compound	Boot Code	Total Boot Weight Grams	Molded Boot Weight Grams	Upper Weight Grams	Outsole Weight Grams	Outsole Specific Gravity	Insert
N-14	L	669	637	380	257	0.674	No
	R	687	657	401	256	0.687	No
N-01S	L	706	679	426*	253	0.682	Yes
	R	683	652	401*	251	0.695	Yes
N-02S	L	679	650	404*	246	0.663	Yes
	R	702	675	423*	251	0.697	Yes
N-03S	L	689	661	408*	253	0.682	Yes
	R	690	662	412*	249	0.691	Yes
N-04S	L	681	652	402*	250	0.675	Yes
	R	695	667	413*	254	0.684	Yes
N-05S	L	678	649	397*	252	0.680	Yes
	R	687	659	407*	252	0.699	Yes
N-06S	L	683	655	401*	254	0.685	Yes
	R	711	678	427*	251	0.695	Yes
N-07S	L	686	659	404*	255	0.686	Yes
	R	701	672	421*	251	0.696	Yes
N-08S	L	690	662	407*	255	0.686	Yes
	R	707	679	427*	252	0.699	Yes
N-09S	L	691	663	411*	252	0.697	Yes
	R	699	669	419*	250	0.692	Yes
N-10S	L	685	658	406*	252	0.681	Yes
	R	688	657	408*	249	0.689	Yes
N-11S	L	700	672	423*	249	0.672	Yes
	R	687	666	416*	250	0.692	Yes
N-12S	L	693	656	405*	253	0.682	Yes
	R	699	668	419*	249	0.689	Yes

* - includes insert weight and in specific gravity computation allowance is made for insert volume

TABLE 16

**PHYSICAL TEST RESULTS ON TEST PANELS MADE
DURING PROCESSING OF FIFTY PAIR OF BOOTS**

Property	Spec.	PTMG (1.0-2.0-0.3-3.3)	
		PTMG	PCP
1. Specific Gravity	0.65 max	0.67	0.69
2. Water Pickup %	3.0 max	2.6	1.0
3. Hardness, Shore A	55 ± 5	68	59
Original	not more than 10 PT chg. not more than 15 PT chg.	67	60
After 70 Hrs/212°F		69	73
Hardness chg. @-0°F			
4. Abrasive Index	70 min.	58	31
Original	70 min.	48	27
After 70 Hrs/212°F			
Compression Set @ 50%	25 ± 5	8.4	9.6
Deflection; 24 hrs. @ RT		26.5*	21.5*
Original %			
After Steam Autoclave	20	215	124
% Change			
6. Cut Growth 50,000 Flexes	200 max.	180	30
Original %	200 max.	0	0
After 70 Hrs/212°F			
7. Compression Deflection	150 ± 10	216	192
@ 25% Deflection		182*	115*
Original psi	20 max.	16	40
After Steam Autoclave psi			
% Change			
Original psi		214	192
After 1 Hr. @ 0°F		181	189
% Change	15% max.	15	15
8. Bond Strength, lbs.	130 min.	145	200

* - Slightly Distorted Samples

V. Conclusion

1. The fabrication of a direct bottomed combat boot outsole made from an expanded liquid polyurethane polymer and adhered to a conventional leather upper can be made utilizing liquid injection molding equipment.
2. Improved hydrolytic stability of cellular urethane outsoles can be accomplished by choice of base polymer, and the most promising were based on PTMG (poly tetra methylene ether glycol) and PCP (polycaprolactone). Other required properties for the combat boot outsole were maintained.
3. Use of LIM (liquid injection molding) equipment offers a method of automating production of lightweight combat boot footwear based on expanded liquid urethane polymers.
4. Modification of the outsole mold design should aid in eliminating flex cracking of outsole, and improvement of fit helped reduce mold flash.
5. Fifty pair of combat boots for wear testing were produced and delivered to the Project Officer.

Appendix A
List of Materials

<u>Material</u>	<u>Chemical Name</u>	<u>Source</u>
Butanediol	1-4 Butanediol	G.A.F. Corp.
Dabco	Triethylene diamine	Air Products & Chemicals, Inc.
Dabco WT	Amine catalyst	Air Products & Chemical, Inc.
DC-193	Silicone surfactant	Dow Corning Co.
Metasol 57 DPG	Mercury catalyst in di propylene glycol	Merck Chemical Co.
MDI	Di phenyl methane diisocyanate	Mobay Chemical Co.
M-420	Quasi-prepolymer	Mobay Chemical Co.
90PC02	Black pigment paste	Harwick Chemical
PCP	Polycaprolactone (2000 MW)	Union Carbide
Polyester Resin	Ethylene glycol adipate (2000 MW)	Mobay Chemical Co.
Polyester Resin	Ethylene butylene adipate (2000 MW)	Mobay Chemical Co.
Polyester 105	Polyester Resin (2000 MW)	Hooker Chemical
Polyester 1015	Polyester Resin (2000 MW)	Hooker Chemical
Polyester 1019	Polyester Resin (2000 MW)	Hooker Chemical
Polyether	Poly tetramethylene ether glycol	Oats Co.
Polyether	Polypropylene glycol package system PPG	Mobay Chemical Co.
Staboxal	Poly substituted di aryl carbodiimide	Mobay Chemical Co.

Appendix A
List of Materials
(continued)

<u>Material</u>	<u>Chemical Name</u>	<u>Source</u>
T-9	Stannous octuate	M & T Chemical
T-12	Dibutyl tin dilaurate	M & T Chemical
3-35	Adipate polyester polyol (pkg)	BASF

Appendix B
Equipment Suppliers

<u>Equipment</u>	<u>Description</u>	<u>Source</u>
Mold	Combat boot outsole	Compo Industries
LIM	Foam metering and mixing	Polyair Machinebau Desma-Werke